



Synthesis and Degradation of a Caged Coumarin Linker

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A critical aspect of designing biomaterial carriers for cells and drug delivery is tuning and controlling the material's degradation behavior. In the last decade, there has been considerable interest in using photochemistry to produce biomaterials because of the ability to form scaffolds in situ under physiological conditions; integrating photochemistry as a degradation mechanism should be equally biocompatible and give spatial and temporal control. In this project, we are synthesizing a model compound that degrades via both single and two-photon photolysis. In single-photon photolysis, any volume exposed to light is susceptible to degradation. Two-photon degradation only occurs where two photons are simultaneously absorbed (the laser focal point), allowing for 3D control over degradation. The model compound contains a nitrobenzyl ether (NBE) moiety linked to a coumarin fluorophore, which imparts two-photon photolysis sensitivity. The model compound also contains two polymerizable groups (acrylates) for network formation. We have synthesized both the NBE linker and the coumarin fluorophore, which will be coupled to form the model compound, 2-(acryloyloxy)-ethyl 7-(1-(4-(4-(2-(acryloyloxy)ethoxy)4-oxobutoxy)-5-methoxy-2-nitrophenyl)ethoxy)-6-chlorocoumarin-3-carboxylate. We will characterize the single-photon degradation of this model compound using long-wave UV light at 365 nm. The degradation will be followed using ^1H NMR spectroscopy. The model compound will be polymerized into a 3D network, which we will spatially pattern in 2D and 3D, using UV light or a two-photon microscope. Photodegradable biomaterials should support on-demand degradation, resulting in a sophisticated platform that allows encapsulation of cells and provides unprecedented external control of the cellular (micro)environment (chemical and physical) in both time and space.

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